Colloids and Surfaces A: Physicochem. Eng. Aspects 442 (2014) 2–5

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Anomalous thickness dependence of nano-composite layer-by-layer membranes

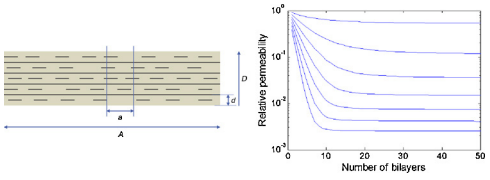
G.J.M. Koper*, K. Vilcinskas

Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

HIGHLIGHTS

- Surface coverage per layer better parameter than fill factor.
- Thickness dependence due to inhomogeneous filler distribution.
- There is a minimal number of layers required for optimal blocking.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 December 2012
Received in revised form
16 September 2013
Accepted 6 December 2013
Available online 19 December 2013

Keywords:
Layer-by-layer deposition
Barrier properties
Composites

ABSTRACT

Homogenous, impermeable platelet dispersions significantly enhance the barrier properties of polymer composite membranes. Layer-by-layer (LbL) deposition allows achieving the highest degree of orientation in comparison to melt blending or solution casting. However, membranes produced by assisted self-assembly, exhibit a strong thickness dependence of their barrier properties. Such behavior could arise from an unevenly dispersed phase distribution in the continuous phase. Here, we analyze this anomalous thickness dependence of gas permeability in platelet–polymer composites produced by the LbL method and on the basis of this result we present a design criterion for these systems.

1. Introduction

The formation of nanocomposites and nanocoatings using layer-by-layer (LbL) assisted self-assembly is widely studied as it is versatile and simple to perform [1]. A variety of coating materials and substrates [1] have been utilized to build-up multilayers for various purposes [1,2] amongst which the inhibition of gas permeation. The formation of composite membranes is of interest here as the manufacturing process is well controlled and because this technique allows one to study some intrinsic properties of composite membranes that would otherwise not be accessible. One such property is the barrier quality of a membrane as is commonly described by means of the permeability, P, which from an experimental point of view can be expressed as the ratio

$$P = \frac{JD}{\Delta pA} \tag{1}$$

where J is the mass flow of gas as a consequence of a pressure difference Δp across the membrane. As the resistance of a membrane is proportional to the thickness D and inversely proportional to the surface area A, the permeability as defined by Eq. (1) is independent of the dimensions of the membrane and solely depends on the material. Indeed, putting two identical membranes in series or parallel renders equivalent permeability values.

Permeation of gas through composite membranes is a complex process, which is thought to consist of a few individual processes: the sorption of diffusing species to the surface, dissolution inside the composite, diffusion through the material, and desorption from the other side of the composite. This complexity is reflected by the large number of models that have been put forward to describe membrane behavior, see [3,4] for a review. Most of them [5–9],

* Corresponding author. Tel.: +31 152788218.
E-mail address: g.j.m.koper@tudelft.nl (G.J.M. Koper).

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.12.016

Table 1
Summary of LbL membranes investigated here for their oxygen transmission reduction properties. Membranes are composed of either polyethylene imine (PEI), polyacrylamide (PA), and Chitosan as polymer matrix and montmorrillonite (MMT), vermiculite (VMT) or graphene oxide (GO) as a filler. The fill factor ϕ is taken from the referred source or calculated from the filler concentration using the mass density, where the mass density for vermiculite and graphene oxide was estimated at 2.5 and 2.3 g/cm^3 respectively. See the text for the zero-layer extrapolated permeability $P(0)$ and the characteristic number of layers $\overline{N}$; P_m is the reference value of 10^{-6} cm^3/(m day atm).

Polymer	Filler	ϕ	$\overline{N}$	$P(0)/P_m$	Reference
PEI	MMT	0.553	10	4.29	[10]
Chitosan	MMT	0.467	4	10.7	[11]
PEI	VMT	0.925	12	0.10	[12]
PA	MMT	0.045	10	0.66	[13]
PEI	GO	0.775	37	0.15	[14]
PEI	GO	0.826	52	0.10	[14]

try to evaluate the transport process by taking into account the different impermeable phase shapes and loading volumes. One of the first attempts to assert gas permeation through polymeric composites was by Nielsen [7], where uniformly dispersed solid platelets of rectangular shape act as impermeable obstacles for the diffusing species. Cussler et al. [5] have expanded Nielsens model by taking into account the flake shape and flake alignment. In both models, the continuous phase is considered as uniform to gas diffusion where the barrier properties are enhanced either by increasing filler loading volume ϕ or the aspect ratio α, i.e. the length to thickness ratio, of the platelets, or both. Many variations on these models, thereby particularly focussing on shape and affinity of the embedded material, have been put forward [3]. The more recent literature [4] concerns the increased gas permeation in the neighborhood of dispersed material due to the modification of the membrane matrix. Another new development is the analysis of the barrier properties of nanocomposite membranes created by the LbL technique [10–14]. These studies reveal an anomalous thickness dependence of their permeability. As discussed above, permeability, is an inherent property of the membrane material and the size and thickness of a membrane, be it a multilayered structure or a single sheet, should not influence its value. However, experimental data demonstrates a totally different picture and the interesting question that we shall try to answer here is: what is the cause of this thickness dependence and how many layers are necessary in order to remove the anomalous thickness dependence.

2. Literature data analysis

We have examined data from various sources [10–14] where composite multilayers were built by dip assisted self-assembly. The synthesis consisted of a few steps. First, the negatively charged substrate was immersed into a solution of cationic polyelectrolyte and a polymer layer was adsorbed as was signalled by a reversal of the charge of the substrate. Then rinsing and drying steps followed after which the coated substrate was immersed into either a negatively charged polyelectrolyte solution or a montmorillonite or graphene oxide dispersion. The procedure was repeated until the desired number of layer was adsorbed.

Although the filler loading volume values differ in these studies, the authors were successful in achieving a brick-like wall structure of filler particles in the polymer matrix and significantly enhanced the barrier properties of the composites, see Table 1. For these membranes, it is typically found that the membrane thickness D increases linearly or even super-linearly with the number of bilayers N. Also, the oxygen permeability P of the nanocomposite membranes was reduced by a few orders of magnitude compared to the bare polymer and increased with the number of adsorbed bilayers N. In Fig. 1 we have plotted the data from all the systems

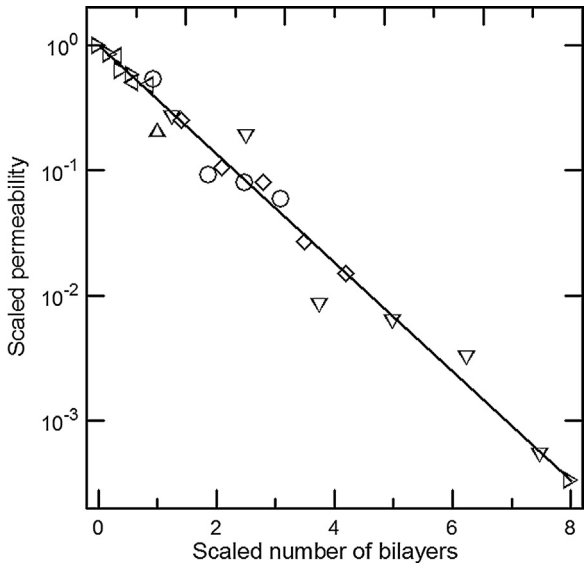


Fig. 1. Scaled representation of the data listed in Table 1: (△) PEI/MMT [10], (▽) Chitosan/MMT [11], (○) PEI/VMT [12], (◇) PA/MMT [13], (▷) PEI/GO low density, and (◁) PEI/GO high density [14]. The trend line is exponential in the scaled number of layers.

listed in Table 1 in a scaled manner confirming a unique trend line that demonstrates that the permeability decays exponentially with the number of layers as

$$P = P(0)\exp\left(\frac{-N}{\overline{N}}\right). \quad (2)$$

The graph in Fig. 1 confirms that the data on gas permeability through LbL membranes exhibits an unpredictable thickness dependence. Even though the volume loading values of the dispersed phase differ in each of the cases, the barrier properties of the membranes show the same behaviour in terms of the thickness increment. Such unexpected behavior could be explained by an uneven impermeable platelet distribution, as will be discussed below.

3. Effect of inhomogeneous filler distribution

We hypothesize that the experimentally found strong dependence of the permeability on the number of layers, as illustrated in Fig. 1, is due to the inhomogeneous distribution of platelets in the layers. This hypothesis is supported by transmission electron micrographs given in the cited articles, e.g. [10,15,12,11], where one easily distinguishes dark and light areas corresponding to clusters of platelets and near voids respectively.

In order to quantify the anomalous thickness dependence we divide such a membrane into individual cells in the lateral direction. The filler numbers n_j differ for each cell j taking values ranging from 0 for no platelet to N, which signifies one platelet in every of the layers. Hence, the mass flow through each of the cells will be different and therefore also permeation varies from cell to cell. The cell surface area is chosen such, that it typically encloses one platelet, see Fig. 2, so that in a regular distribution it would be equal to the unit cell.

Let us first discuss the platelet distribution in a single membrane layer in relation to the overall fill factor. The membrane has a surface area A, see Fig. 2. The platelet surface area σ is much smaller so that quite a number of platelets is needed to cover the total surface area. The fill factor of the layer is given by

$$\phi = \frac{M\sigma\delta}{Ad} \quad (3)$$